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**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)**

INTERNATIONAL APPLICATION NO.
PCT/EP00/09246

INTERNATIONAL FILING DATE
21/09/2000
(21 September 2000)

PRIORITY DATE CLAIMED
23/09/1999
(23 September 1999)

TITLE OF INVENTION

Utilization of Water-Soluble Zirconium Compounds as Drying Accelerators in Aqueous Coating Agents


APPLICANT(S) FOR DO/EO/US: Thomas FICHTNER

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items under 35 U.S.C. 371:

1. ☒ This express request to immediately begin national examination procedures (35 U.S.C. 371(f)).
2. ☒ The U.S. National Fee (35 U.S.C. 371(c)(1)) and other fees as follows:

| CLAIMS | (1) FOR | (2) NUMBER FILED | (3) NUMBER EXTRA | (4) RATE | (5) CALCULATIONS |
|--------|--|---------------------|---------------------|---|---------------------|
| | TOTAL CLAIMS | 22 - 20 = | 2 | X \$18.00 | 36.00 |
| | INDEPENDENT CLAIMS | 2- 3 = | 0 | X \$84.00 | |
| | MULTIPLE DEPENDENT CLAIMS (if applicable) | | | + 280.00 | |
| | BASIC NATIONAL FEE (37 CFR 1.492(a) (1)-(4): <input checked="" type="checkbox"/> For filing with EPO or JP search report (37 CFR 1.492(a)(5) International Preliminary Examination fee paid to USPTO (37 CFR 1.482) No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) Neither international preliminary examination fee paid to USPTO (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Articles 33(2)-33(4) | | | \$ 890.00 740.00 710.00 1,040.00 100.00 | 890.00 |
| | Surcharge of \$135.00 for furnishing the National fee or oath or declaration later than <u>20</u> <u>30</u> months from the earliest claimed priority date (37 CFR 1.492(e)). | | | | |
| | TOTAL OF ABOVE CALCULATIONS | | | | = \$ 926.00 |
| | SUBTOTAL | | | | + \$ 926.00 |
| | Processing fee of \$135.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). | | | | |
| | TOTAL NATIONAL FEE | | | | \$926.00 |
| | Fee for recording the enclosed assignment (37 CFR 1.21(h)). | | | | + 0.00 |
| | TOTAL FEES ENCLOSED | | | | \$926.00 |

- a. ☒ Please charge my Deposit Account No. 03-2060 in the amount of \$ 926.00 to cover the above fees. A duplicate copy of this sheet is enclosed.
- b. ☒ The Commissioner is authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 03-2060. A duplicate copy of this sheet is enclosed.

| | | | | |
|---|-------------------------------------|--|---|--|
| 3. | <input checked="" type="checkbox"/> | A copy of the International Application as filed (35 USC 371(c)(2)) | | 10/088828 |
| | | a. | <input type="checkbox"/> | is transmitted herewith (required only if not transmitted by the International Bureau) and English translation |
| | | b. | <input type="checkbox"/> | is not required, as the application was filed in the US Receiving Office (RO/US) |
| | | c. | <input checked="" type="checkbox"/> | has been transmitted by the International Bureau. |
| 4. | <input checked="" type="checkbox"/> | A translation of the International Application into English (35 USC 371(c)(2)). | | |
| 5. | | Amendments to the claims of the International Application under PCT Article 19 (35 USC 371(c)(3)). | | |
| | | a | <input type="checkbox"/> | Are transmitted herewith (required only if not transmitted the International Bureau) |
| | | b. | <input type="checkbox"/> | Have been transmitted by the International Bureau. |
| 6. | | A translation of the amendments to the claims under PCT Article 19 (35 USC 371(c)(3)). | | |
| 7. | | An oath or declaration of the inventor (35 USC 371(c)(4)). | | |
| 8. | <input checked="" type="checkbox"/> | A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 USC 371(c)(5)). | | |
| Other document(s) or information included: | | | | |
| 9. | | An information Disclosure Statement under 37 CFR 1.97 and 1.98. | | |
| 10. | | An assignment document for recording. Please mail the recorded assignment document to the person whose signature, name and address appears at the bottom of this page. | | |
| 10.1 | | A copy of the International Filing Receipt. | | |
| 10.2 | | A copy of the International Search Report. | | |
| 10.3 | <input checked="" type="checkbox"/> | A copy of the International Preliminary Examination Report. | | |
| 10.4 | | A copy of Form PCT/IB/306 - Notification of the Recording of a Change | | |
| 10.5 | <input checked="" type="checkbox"/> | Preliminary Amendment. | | |
| 11. | <input checked="" type="checkbox"/> | The above checked items are being transmitted: | | |
| | | <input checked="" type="checkbox"/> | by thirty (30) months and a proper demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. | |
| 12. | | At the time of transmittal, the time limit for amending claims under Article 19: | | |
| | | a. | <input checked="" type="checkbox"/> | has expired and no amendments were made. |
| | | b. | <input type="checkbox"/> | has not yet expired. |
| 13. | | Certain requirements under 35 USC 371 were previously submitted by the applicant on _____, namely: | | |
| <div><div> Anthony A. Bisulda, Registration No. 40,913 Clariant Corporation 4331 Chesapeake Drive Charlotte, North Carolina 28216 Telephone: 704/395-6701 Facsimile: 704/395-6727</div><div>Date: March 22, 2002</div></div> | | | | |

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Thomas FICHTNER

Docket: 1999DE508

Serial No.: to be assigned

Filed: March 22, 2002

For: UTILIZATION OF WATER-SOLUBLE ZIRCONIUM COMPOUNDS AS
DRYING ACCELERATORS IN AQUEOUS COATING AGENTS**PRELIMINARY AMENDMENT**Assistant Commissioner for Patents
Washington, D.C. 20231

Dear Sir:

Prior to the calculation of the filing fee for the above-identified application, please amend the application as follows:

In the Claims


Please amend claims 1-12 as follows:

1. (Amended) A method for accelerating the drying of an aqueous coating composition having one or more binders comprising the step of adding one or more water-soluble zirconium compounds to the coating composition, wherein the binders present in the coating composition include polymer dispersions based on one or more homopolymers and/or copolymers.
2. (Amended) The method as claimed in claim 1, wherein the overall zirconium compound content, calculated as zirconium oxide and based on the binders present in the coating composition, is up to 50% by weight.

CERTIFICATION UNDER 37 CFR 1.10Express Mail Label No. ET825363348US

Date of Mailing: March 22, 2002

I hereby certify that on the date indicated above, this new U.S. patent application and the papers indicated as enclosed therein, is being deposited with the United States Postal Service as "Express Mail Post Office to Addressee" addressed to: Assistant Commissioner for Patents, Box PCT DO/EO/US, Washington, D.C. 20231, in accordance with 37 CFR 1.10.



Signature of Person Mailing the ApplicationVicki L. Sgro

Typed Name of Person Mailing the Application

3. (Amended) The method as claimed in claim 2, wherein the overall zirconium compound content is from 0.5 to 10% by weight.
4. (Amended) The method as claimed in claim 1, wherein the one or more water-soluble zirconium compounds is selected from the group consisting of ammonium zirconium carbonate, zirconium acetoacetate, zirconium hydroxychloride, zirconium orthosulfate, zirconium propionate and potassium zirconium phosphate.
5. (Amended) The method as claimed in claim 4, wherein the one or more water-soluble zirconium compounds is ammonium zirconium carbonate.
6. (Amended) The method as claimed in claim 1, wherein the one or more zirconium compounds are added to the coating composition as solids and/or as aqueous solutions.
7. (Amended) The method as claimed in claim 1, wherein the coating composition includes at least one additive, wherein the at least one additive is selected from the group consisting of film formers, pigments, fillers, thickeners, dispersants, wetting agents, preservatives, emulsifiers and defoamers.
8. (Amended) The method as claimed in claim 1, wherein, based on the overall amount of the monomers, the copolymers comprise:
 - a) from 70 to 99.7% by weight of one or more free-radically polymerizable olefinically unsaturated compounds selected from the group consisting of acrylates and methacrylates of (C₁-C₁₂) monoalcohols, vinylaromatic monomers, vinyl esters of (C₁-C₁₂) alkanemonocarboxylic acids, vinyl halides, α,β -monoolefinically unsaturated nitriles and alkyl esters of monoolefinically unsaturated dicarboxylic acids,

- b) from 0.3 to 10% by weight of one or more compounds selected from the group consisting of α,β -monoolefinically unsaturated monocarboxylic acids, dicarboxylic acids, and their amides or N-substituted amides, and
 - c) from 0 to 20% by weight of compounds selected from the group consisting of hydroxyl-containing monomers, acetylacetoxy-containing monomers, monomers containing epoxide groups, monomers containing silane groups, nitrogen-containing monomers and monomers containing keto groups.
9. (Amended) The method as claimed in claim 1, wherein the one or more binders comprise at least one additive selected from the group consisting of emulsifiers, protective colloids, additives, auxiliaries and noncopolymerizable crosslinkers.
 10. (Amended) The method as claimed in claim 1, wherein the aqueous coating composition is a composition selected from the group consisting of an exterior paint, an interior paint, a roadmarking paint, a primer, a wood coating, exterior render and interior plaster.
 11. (Amended) The method as claimed in claim 1, wherein the aqueous coating composition is a composition selected from the group consisting of adhesives, pastes, putties, sealing compounds and pressure compensation coatings for exterior insulation and finish systems.
 12. (Amended) The method as claimed in claim 1, wherein the coating composition includes unadditived binders.

Please add new claims 13 through 22 as follows:

17. (New) A paint comprising the aqueous coating composition as claimed in claim 13.
18. (New) A primer comprising the aqueous coating composition as claimed in claim 13.
19. (New) A wood coating comprising the aqueous coating composition as claimed in claim 13.
20. (New) An exterior render comprising the aqueous coating composition as claimed in claim 13.
21. (New) An interior plaster comprising the aqueous coating composition as claimed in claim 13.
22. (New) A compound comprising the aqueous coating composition as claimed in claim 13, wherein the compound is selected from the group consisting of adhesives, pastes, putties, sealing compounds and pressure compensation coatings for exterior insulation and finish systems

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Thomas FICHTNER

Docket: 1999DE508

Serial No.: to be assigned

Filed: March 22, 2002

For: UTILIZATION OF WATER-SOLUBLE ZIRCONIUM COMPOUNDS AS
DRYING ACCELERATORS IN AQUEOUS COATING AGENTS

Version with Markings to Show Changes Made

IN THE CLAIMS

Please amend claims 1-12 as follows:

1. (Amended) A method for accelerating the drying of an aqueous coating composition having one or more binders comprising the step of adding [The use of] one or more water-soluble zirconium compounds to the coating composition [as drying accelerators in aqueous coating compositions], wherein the binders present in the coating [compositions comprising] composition include polymer dispersions based on one or more homopolymers and/or copolymers.
2. (Amended) The [use] method as claimed in claim 1, [characterized in that] wherein the overall zirconium compound content, calculated as zirconium oxide and based on the binders present in the coating [compositions] composition, is up to 50% by weight.
3. (Amended) The [use] method as claimed in claim 2, [characterized in that] wherein the overall zirconium compound content is from 0.5 to 10% by weight.

4. (Amended) The [use] method as claimed in [at least one of the preceding claims, characterized in that the zirconium compounds] claim 1, wherein the one or more water-soluble zirconium compounds is selected from the group consisting of [used comprise] ammonium zirconium carbonate, zirconium acetoacetate, zirconium hydroxychloride, zirconium orthosulfate, zirconium propionate and[/or] potassium zirconium phosphate.
5. (Amended) The [use] method as claimed in claim 4, [characterized in that] wherein the one or more water-soluble zirconium compounds is ammonium zirconium carbonate [is used as zirconium compound].
6. (Amended) The [use] method as claimed in [at least one of the preceding claims, characterized in that] claim 1, wherein the one or more zirconium compounds are added to the coating [compositions] composition as solids and/or as aqueous solutions.
7. (Amended) The [use] method as claimed in [at least one of the preceding claims, characterized in that in addition to the binder] claim 1, wherein the coating [compositions comprise] composition includes at least one additive, wherein the at least one additive is selected from the group consisting of film formers, pigments, fillers, thickeners, dispersants, wetting agents, preservatives, emulsifiers and[/or] defoamers.
8. (Amended) The [use] method as claimed in [at least one of the preceding claims, characterized in that,] claim 1, wherein, based on the overall amount of the monomers, the copolymers [contain] comprise:
 - a) from 70 to 99.7% by weight of one or more free-radically polymerizable olefinically unsaturated compounds selected from the group

consisting of acrylates and methacrylates of (C₁-C₁₂) monoalcohols, vinylaromatic monomers, vinyl esters of (C₁-C₁₂) alkanemonocarboxylic acids, vinyl halides, α,β -monoolefinically unsaturated nitriles and[/or] alkyl esters of monoolefinically unsaturated dicarboxylic acids,

b) from 0.3 to 10% by weight of one or more compounds selected from the group consisting of α,β -monoolefinically unsaturated monocarboxylic acids, [and] dicarboxylic acids, and[/or] their amides or N-substituted amides, and

c) from 0 to 20% by weight of compounds selected from the group consisting of hydroxyl-containing monomers, acetylacetoxy-containing monomers, monomers containing epoxide groups, monomers containing silane groups, nitrogen-containing monomers and[/or] monomers containing keto groups.

9. (Amended) The [use] method as claimed in [at least one of the preceding claims, characterized in that] claim 1, wherein the one or more binders comprise at least one additive selected from the group consisting of emulsifiers, protective colloids, additives, auxiliaries and[/or] noncopolymerizable crosslinkers.
10. (Amended) The [use] method as claimed in [at least one of the preceding claims, characterized] claim 1, wherein the aqueous coating composition is a composition selected from the group consisting of [in that the coating compositions comprise] an exterior paint, an interior paint, a roadmarking paint, a primer, a wood coating, exterior render [or] and interior plaster.
11. (Amended) The [use] method as claimed in [at least one of claims 1 to 9, characterized in that] claim 1, wherein the aqueous coating [compositions comprise] composition is a composition selected from the group consisting

12. (Amended) The [use] method as claimed in [at least one of claims 1 to 9, characterized in that] claim 1, wherein the coating [compositions] composition [comprise the] includes unadditived binders [which are used as they are].

13. (New) An aqueous coating composition comprising:
at least one binder, wherein the at least one binder includes polymer
dispersions based on one or more homopolymers and/or copolymers; and
at least one water-soluble zirconium compound.

14. (New) The aqueous coating composition as claimed in claim 13, wherein the at least one zirconium compound is present in an amount up to 50% by weight, calculated as zirconium oxide and based on the at least one binder present in the coating composition.

15. (New) The aqueous coating composition as claimed in claim 13, wherein the at least one zirconium compound is selected from the group consisting of ammonium zirconium carbonate, zirconium acetoacetate, zirconium hydroxychloride, zirconium orthosulfate, zirconium propionate and potassium zirconium phosphate.

16. (New) The aqueous coating composition as claimed in claim 13, wherein based on the amount of monomers, the copolymers comprise:

- a) from 70 to 99.7% by weight of one or more free-radically polymerizable olefinically unsaturated compounds selected from the group consisting of acrylates and methacrylates of (C₁-C₁₂) monoalcohols, vinylaromatic monomers, vinyl esters of (C₁-C₁₂) alkanemonocarboxylic acids, vinyl halides, α,β -monoolefinically unsaturated nitriles and alkyl esters of monoolefinically unsaturated dicarboxylic acids,
 - b) from 0.3 to 10% by weight of one or more compounds selected from the group consisting of α,β -monoolefinically unsaturated monocarboxylic acids, dicarboxylic acids, and their amides or N-substituted amides, and
 - c) from 0 to 20% by weight of compounds selected from the group consisting of hydroxyl-containing monomers, acetylacetoxy-containing monomers, monomers containing epoxide groups, monomers containing silane groups, nitrogen-containing monomers and monomers containing keto groups.
17. (New) A paint comprising the aqueous coating composition as claimed in claim 13.
18. (New) A primer comprising the aqueous coating composition as claimed in claim 13.
19. (New) A wood coating comprising the aqueous coating composition as claimed in claim 13.
20. (New) An exterior render comprising the aqueous coating composition as claimed in claim 13.
21. (New) An interior plaster comprising the aqueous coating composition as claimed in claim 13.

22. (New) A compound comprising the aqueous coating composition as claimed in claim 13, wherein the compound is selected from the group consisting of adhesives, pastes, putties, sealing compounds and pressure compensation coatings for exterior insulation and finish systems

Utilization Of Water-Soluble Zirconium Compounds As Drying Accelerators In Aqueous Coating Agents

The present invention relates to the use of water-soluble zirconium compounds as drying accelerators in aqueous coating compositions.

Conventional systems for quick-drying coatings are generally solventborne. In these solvent-based coating compositions, the rate of drying can be controlled by varying the solids content and/or the solvent. Aqueous coating compositions are environmentally friendly and in recent times have come more and more to replace their solvent-based counterparts. For preparing a waterborne coating composition, it is normal to use polymer dispersions as the binder.

A disadvantage of aqueous coating compositions is the dependence of the drying rate on the temperature and atmospheric humidity. At low atmospheric humidity the drying rate is generally quick, in some cases even quicker than in the case of conventional coating compositions. At high atmospheric humidities and low temperatures, however, such as in the morning and evening, for example, and before or after rainfall, the drying rate is very slow, since the evaporation of the water is greatly hindered. Such coatings then acquire rain resistance only after very long standing times. Accelerated drying of aqueous coating compositions is desirable particularly for exterior applications, such as, for example, paints for buildings, bridges, ships, and road markings, and also exterior renders.

For quick-drying aqueous coating compositions there are three different principles possessing practical relevance.

According to the flocculation principle, flocculation of the ionically stabilized binder takes place either following application of the coating composition,

which comprises a polyamine and ammonia as volatile base, as a result of the fact that the ammonia evaporates (US-A-5 527 853, EP-A-0 594 321, EP-A-0 728 822, EP-A-0 409 459) or by virtue of the fact that, together with the coating composition, an acid solution (WO 94/29 391) or a salt solution (EP-A-0 200 249, US-A-4 571 415, US-A-5 403 393) is sprayed.

A change in viscosity of the surface of the coating composition can be brought about by applying either a thickener to the fresh coating, thereby producing an increase in viscosity, as disclosed, for example, in EP-A-0 721 003, or a base to the fresh coating which comprises a thickener which, however, is not activated by formulation of a low pH.

In the case of a water absorption method, water-absorbing substances, such as silica gels, ion exchangers, polymer gels, etc., are used during the application of the coating composition.

In the case of coating compositions where drying is activated by evaporation of a volatile base such as ammonia, the scope of application is limited as a result, for example, of odor pollution. Coating compositions which are brought into contact with salts following their application have the disadvantage of being restricted to the use of weakly stabilized dispersions. The salts used must be sprayed as a solution together with the coating composition or applied subsequently by spraying or scattering. In the case of subsequent application of the salts in solid or dissolved form, considerable fractions may be washed away by rain, for example, thereby severely impairing the efficiency of the method. The quantities of salt washed away by rain generally pass into the groundwater. Consequently, this mode of drying is undesirable.

EP-A-0 709 441 discloses the use of zirconium compounds in paints and adhesives. The zirconium compounds there are used as a siccative, crosslinking reagent, thixotropic agent, free-radical scavenger in

decomposition reactions of coating films, and a complexing substance for ingredients which normally lead to bleeding and/or discoloration of surfaces.

It has surprisingly now been found that coating compositions which comprise one or more water-soluble zirconium compounds exhibit markedly accelerated drying. In particular, they do so even at low temperatures. The binders present in the coating compositions are, surprisingly, not subject to any special requirements.

For use in accordance with the invention the coating compositions contain, based on the binder, preferably up to 50% by weight, with particular preference from 0.5 to 10% by weight, and in particular from 1 to 5% by weight of zirconium compounds, calculated as zirconium oxide.

Zirconium compounds used are preferably ammonium zirconium carbonate, zirconium acetoacetate, zirconium hydroxychloride, zirconium orthosulfate, zirconium propionate and/or potassium zirconium phosphate. Particular preference is given to using ammonium zirconium carbonate.

The zirconium compounds may be added to the coating composition as solids and/or as aqueous solutions.

In addition to a binder, the zirconium-containing coating compositions may when appropriate further comprise film formers, pigments, fillers (such as titanium dioxide, talc, calcite, dolomite, for example), thickeners (such as cellulose ethers, acrylic acid, polyurethane thickeners, for example), dispersants, wetting agents, preservatives, emulsifiers and/or defoamers. The pigment volume concentration (PVC) is generally situated between 15 and 90%. In order to increase the stability of the coating composition it is possible where appropriate additionally for from 0.1 to 5% by weight, preferably from

0.5 to 1% by weight, based on the binder, of ionic and/or nonionic emulsifiers to be added to it.

The binders present in the coating compositions generally comprise polymer dispersions based on homopolymers and/or copolymers. Suitable homopolymers and copolymers include all known homopolymers and copolymers which are obtainable in dispersion form.

In one preferred embodiment the copolymers contain from 70 to 99.7% by weight, based on the overall amount of the monomers, of free-radically polymerizable olefinically unsaturated compounds from the group consisting of acrylates and methacrylates of (C₁-C₁₂) monoalcohols, preferably of (C₁-C₈) monoalcohols, examples being methanol, ethanol, isopropanol, isobutanol, n-butanol, and 2-ethylhexyl alcohol, vinylaromatic monomers, vinyl esters of (C₁-C₁₂) alkanemonocarboxylic acids, examples being vinyl acetate, vinyl propionate, vinyl n-butyrate, vinyl laurate, [®]VeoVa 9 and [®]VeoVa 10 (Shell-Chemie, vinyl esters of α,α -dialkyl-branched monocarboxylic acids), vinyl halides, examples being vinyl chloride and vinylidene chloride, α,β -monoolefinically unsaturated nitriles, examples being acrylonitrile and methacrylonitrile, and the alkyl esters of monoolefinically unsaturated dicarboxylic acids, examples being di-n-butyl maleate and di-n-butyl fumarate.

The copolymers further contain preferably from 0.3 to 10% by weight, with particular preference from 0.5 to 5% by weight, based on the overall amount of the monomers, of α,β -monoolefinically unsaturated monocarboxylic and dicarboxylic acids, examples being acrylic acid, methacrylic acid, itaconic acid, maleic acid, and fumaric acid, and their amides with or without substitution on the nitrogen atoms, examples being acrylamide, methacrylamide, N-methylolacrylamide and N-butoxymethacrylamide.

It is also possible for from 0 to 20% by weight, preferably from 0.5 to 5% by weight, based on the overall amount of the monomers, of functional monomers to be present in the copolymers, examples being hydroxyl-containing monomers, such as hydroxyalkyl acrylates and methacrylates, especially hydroxyethyl methacrylate and hydroxypropyl methacrylate, and/or acetylacetoxy-containing monomers which improve the wet adhesion, particularly allyl acetoacetate, acetylacetoxyethyl methacrylate and acetylacetoxybutyl methacrylate, and/or monomers with a crosslinking action such as monomers containing epoxide groups and monomers containing silane groups, particular glycidyl acrylate, glycidyl methacrylate, vinyltrimethoxysilane and methacryloyloxypropyltrimethoxysilane, and/or nitrogen-containing monomers from the group consisting of polymerizable monomers containing an amino, ureido or n-heterocyclic group, examples being dimethylaminoethyl acrylate and dimethylaminoethyl methacrylate, N-(2-methacryloylethyl)ethyleneurea, and/or monomers containing keto groups, examples being diacetone acrylamide, diacetone methacrylamide, acrolein, and 2-butanone methacrylate.

In self-crosslinking dispersions, polymers containing keto groups may also contain up to 5% by weight, based on the overall amount of the monomers, of a difunctional or polyfunctional carboxylic hydrazide, an example being adipic hydrazide.

The binders may where appropriate further comprise emulsifiers, protective colloids, additives, auxiliaries and/or noncopolymerizable crosslinkers.

Examples of suitable nonionic emulsifiers include alkyl polyglycol ethers and ethoxylation products of polypropylene oxide. Suitable ionogenic emulsifiers include primarily anionic emulsifiers, such as alkali metal salts or ammonium

Suitable protective colloids include natural substances, such as gum arabic, starch, and alginates, for example, or modified natural substances, such as cellulose derivatives, for example, or synthetic polymers, such as polyvinyl alcohol and polyvinylpyrrolidone, for example, or mixtures thereof.

In the widest sense, the coating compositions of the present invention may also comprise adhesives, pastes, putties, sealing compounds or pressure compensation coatings for exterior insulation and finish systems.

The invention is described in more detail below with reference to examples, without being restricted thereby.

The synthetic-resin renders described in the inventive and comparative examples have the base formula indicated in Table 1.

Preparation of a comparative render 1 containing no zirconium compound

To prepare the render, the water is introduced initially and the remaining ingredients are added in the order stated, with mixing. After the raw materials have been introduced, the render is mixed until completely homogeneous.

Table 1: Base formula of a synthetic-resin render

| Ingredients | Parts by weight |
|---|-----------------|
| 1. Water | 56.9 |
| 2. Cellulose ether (type MC, medium viscosity) | 1.5 |
| 3. Dispersant (polyacrylate) | 3.0 |
| 4. Preservative (isothiazolinone) | 2.0 |
| 5. Wetting agent (polyphosphate) | 0.6 |
| 6. Sodium hydroxide solution, 10% | 2.0 |
| 7. Defoamer (based on mineral oil) | 2.0 |
| 8. Synthetic-resin dispersion | 140.0 |
| 9. Pigment (titanium dioxide) | 20.0 |
| 10. Filler (kaolin 3 μm) | 20.0 |
| 11. Filler (calcite particle size 40 μm) | 150.0 |
| 12. Filler (calcite particle size 130 μm) | 170.0 |
| 13. Filler (calcite 130 μm – 500 μm) | 100.0 |
| 14. Texturing grain (calcite 1.5 – 2.0 mm) | 300.0 |

| | |
|---|-------|
| 15. Auxiliary film former (aliphatic hydrocarbon) | 4.0 |
| 16. Auxiliary film former (glycol ether) | 6.0 |
| 17. Fiber (polyethylene) | 2.0 |
| | 980.0 |

Example 1:

Preparation of a zirconium-containing synthetic-resin render 1.

The composition of synthetic-resin render 1 differs from the base formula indicated in Table 1 only in that it further contains 20 parts by weight of a zirconium compound Bozefix PAS5200 from Clariant GmbH. The binder used is the same synthetic-resin dispersion as in comparative example 1.

To prepare the render, the water is introduced and the remaining ingredients are added in the order stated, with mixing, the zirconium compound being added last. After the raw materials have been introduced, the render is mixed until completely homogeneous.

Comparative example 2:

Preparation of a comparative render 2 containing no zirconium compound.

The composition of comparative render 2 corresponds to the base formula indicated in Table 1 with the binder used being a synthetic-resin dispersion Mowilith® LDM 1880 (Table 1, ingredient 8) from Clariant GmbH having a solids content of 55%, a pH of 5 and a viscosity of 2000 mPas. The monomer basis of this dispersion is formed by vinyl acetate and ethylene. Comparative render 2 is prepared in the same way as comparative render 1 as described in comparative example 1.

Example 2:

Preparation of a zirconium-containing synthetic-resin render 2.

To prepare the render, the water is introduced and the remaining ingredients are added in the order stated, with mixing, the zirconium compound being added last. After the raw materials have been introduced, the render is mixed until completely homogeneous.

a) Preparation of test specimens

b) Testing of the test specimens

After different drying times at a test temperature of 5°C, the test specimens are examined for their degree of drying. To this end the test specimens are each sprayed with 60 grams of water. The water mist is generated using a commercial atomizer. During the spraying operation, the test specimens are situated upright. The liquid running off is collected quantitatively. While the coating composition has not yet dried, the test liquid washes particles out, and as a result acquires a whitish discoloration. The intensity of discoloration allows conclusions to be drawn about the drying state of the coating composition.

The degree of drying of the renders is assessed in accordance with the 6 classes listed in Table 2.

Table 2: Classification of the degrees of drying

| Class | Degree of drying | Coloration of the test liquid |
|-------|------------------|-------------------------------|
| 1 | Dry | No coloration |
| 2 | Almost dry | Slight clouding |
| 3 | Partly dry | Clouding |
| 4 | Damp | Severe clouding |
| 5 | Wet | White |
| 6 | Very wet | Very white |

The degrees of drying of comparative renders 1 and 2 and of synthetic-renders 1 and 2 in accordance with the 6 classes of Table 2 after 4 and 7 hours' drying time at a drying temperature of 5°C are indicated in Table 3.

Table 3: Degrees of drying of the renders investigated

| Coating composition | Degree of drying after 4 hours' drying time | Degree of drying after 7 hours' drying time |
|--------------------------|---|---|
| Comparative render 1 | 4 | 2 to 3 |
| Synthetic-resin render 1 | 2 | 1 to 2 |
| Comparative render 2 | 3 | 2 |
| Synthetic-resin render 2 | 2 | 1 |

As is evident from Table 3, the zirconium-containing synthetic-resin renders 1 and 2 exhibit in every case a higher degree of drying than the comparative renders 1 and 2, irrespective of the binder (synthetic-resin renders 1 and 2 contain different synthetic-resin dispersion binders) and irrespective of the drying time.

Claims:

1. The use of one or more water-soluble zirconium compounds as drying accelerators in aqueous coating compositions, the binders present in the coating compositions comprising polymer dispersions based on one or more homopolymers and/or copolymers.
2. The use as claimed in claim 1, characterized in that the overall zirconium compound content, calculated as zirconium oxide and based on the binders present in the coating compositions, is up to 50% by weight.
3. The use as claimed in claim 2, characterized in that the overall zirconium compound content is from 0.5 to 10% by weight.
4. The use as claimed in at least one of the preceding claims, characterized in that the zirconium compounds used comprise ammonium zirconium carbonate, zirconium acetoacetate, zirconium hydroxychloride, zirconium orthosulfate, zirconium propionate and/or potassium zirconium phosphate.
5. The use as claimed in claim 4, characterized in that ammonium zirconium carbonate is used as zirconium compound.
6. The use as claimed in at least one of the preceding claims, characterized in that the zirconium compounds are added to the coating compositions as solids and/or as aqueous solutions.
7. The use as claimed in at least one of the preceding claims, characterized in that in addition to the binder the coating compositions comprise film formers, pigments, fillers, thickeners, dispersants, wetting agents, preservatives, emulsifiers and/or defoamers.

8. The use as claimed in at least one of the preceding claims, characterized in that, based on the overall amount of the monomers, the copolymers contain
- a) from 70 to 99.7% by weight of one or more free-radically polymerizable olefinically unsaturated compounds from the group consisting of acrylates and methacrylates of (C₁-C₁₂) monoalcohols, vinylaromatic monomers, vinyl esters of (C₁-C₁₂) alkanemonocarboxylic acids, vinyl halides, α,β -monoolefinically unsaturated nitriles and/or alkyl esters of monoolefinically unsaturated dicarboxylic acids,
 - b) from 0.3 to 10% by weight of one or more compounds from the group consisting of α,β -monoolefinically unsaturated monocarboxylic and dicarboxylic acids, and/or their amides or N-substituted amides, and
 - c) from 0 to 20% by weight of compounds from the group consisting of hydroxyl-containing monomers, acetylacetoxy-containing monomers, monomers containing epoxide groups, monomers containing silane groups, nitrogen-containing monomers and/or monomers containing keto groups.
9. The use as claimed in at least one of the preceding claims, characterized in that the binders comprise emulsifiers, protective colloids, additives, auxiliaries and/or noncopolymerizable crosslinkers.
10. The use as claimed in at least one of the preceding claims, characterized in that the coating compositions comprise an exterior paint, an interior paint, a roadmarking paint, a primer, a wood coating, exterior render or interior plaster.

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11. The use as claimed in at least one of claims 1 to 9, characterized in that the coating compositions comprise adhesives, pastes, putties, sealing compounds or pressure compensation coatings for exterior insulation and finish systems.
12. The use as claimed in at least one of claims 1 to 9, characterized in that the coating compositions comprise the unadditived binders which are used as they are.

AMENDED SHEET

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES
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Abkürzungen wird auf die Erklärungen ("Guidance Notes on
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(54) Title: UTILIZATION OF WATER-SOLUBLE ZIRCONIUM COMPOUNDS AS DRYING ACCELERATORS IN AQUEOUS
COATING AGENTS

(54) Bezeichnung: VERWENDUNG VON WASSERLÖSLICHEN ZIRKONVERBINDUNGEN ALS TROCKNUNGSBE-
SCHLEUNIGER IN WÄSSRIGEN BESCHICHTUNGSMITTELN

(57) Abstract: The invention relates to utilization of water-soluble zirconium compounds as drying accelerators in aqueous coating
agents. Particularly suitable zirconium compounds are preferably compounds such as ammonium zirconium carbonate, zirconium
acetoacetate, zirconium hydroxychloride, zirconium orthosulfate, zirconium propionate and potassium zirconium phosphate. Said
coating agents are preferably dyes and plasters.

(57) Zusammenfassung: Die vorliegende Erfindung betrifft die Verwendung von wasserlöslichen Zirkonverbindungen als Trock-
nungsbeschleuniger in wässrigen Beschichtungsmitteln. Als Zirkonverbindungen eignen sich dabei vorzugsweise Verbindungen wie
Ammoniumzirkoncarbonat, Zirkoniumacetatoacetat, Zirkoniumhydroxychlorid, Zirkoniumorthosulfat, Zirkoniumpropionat und Ka-
liumzirkoniumphosphat. Vorzugsweise handelt es sich bei den Beschichtungsmitteln um Farben und Putze.

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1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below, I believe I am the original, first and sole inventor (If only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Utilization of water-soluble zirconium compounds as drying accelerators in aqueous coating agents

the specification of which

☐ is attached hereto

☒ was filed on September 21, 2000, as International Patent Application PCT/EP00/09246

and including all the amendments through the date hereof.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s) for which Priority Is Claimed:

Federal Republic of Germany, 199 45 626.7, of September 23, 1999

As a named inventor, I hereby appoint the following registered practitioner(s), respectively and individually, as my attorneys and/or agents, with full power of substitution and revocation, to prosecute this application, and transact all business in the U.S. Patent and Trademark Office:



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PATENT TRADEMARK OFFICE

Please address all communications to Clariant Corporation, Industrial Property Department, 4331 Chesapeake Drive, Charlotte, North Carolina 28216, telephone number 704/395-6712, facsimile number 704/395-6727.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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